PB84-165034

# EPA (Environmental Protection Agency) Recommended Practice for Naming I/M (Inspection/Maintenance) Calibration Gas A Discussion for I/M Programs

(U.S.) Environmental Protection Agency
Ann Arbor, MI

Sep 83

U.S. Department of Commerce
National Technical Information Service
NTIS.

## TECHNICAL REPORT DATA
*(Please read Instructions on the reverse before completing)*

| 1. REPORT NO. | 2. | 3. RECIPIENT'S ACCESSION NO. |
|---|---|---|
| EPA-AA-TSS-83-8A | | PB84 165034 |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| EPA Recommended Practice for Naming I/M Calibration Gas: A Discussion For I/M Programs. | September 1983 |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>U. S. Environmental Protection Agency<br>Office of Mobile Sources<br>Technical Support Staff<br>Ann Arbor, MI 48105 | 10. PROGRAM ELEMENT NO. |
| | 11. CONTRACT/GRANT NO. |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Same as box 9 | 13. TYPE OF REPORT AND PERIOD COVERED |
| | 14. SPONSORING AGENCY CODE |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This volume of a two-volume report explains how calibration gases are used in Inspection and Maintenance (I/M) programs, and introduces a Recommended Practice for gas manufacturers to use when naming I/M calibration gas cylinders.

Details of the Recommended Practice are presented in a separate report entitled "Recommended Practice for Naming I/M Calibration Gases", (EPA-AA-TSS-83-8B). States are encouraged to procure gases named according to this Recommended Practice for their own use, and to require licensed inspection stations to procure them to ensure that they are obtaining accurate calibration gases which meet the terms of the Emission Control System Performance Warranty, and to improve the general quality of their Inspection and Maintenance programs.

(PB84-165042)

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Air Pollution<br>Exhaust Emissions<br>Gases<br>Inspection<br>Maintenance<br>Motor Vehicles | I/M<br>Regulations<br>Standards<br>State Government | |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES |
|---|---|---|
| Release Unlimited | unclassified | 18 |
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |
| | unclassified | |

EPA Form 2220-1 (9-73)

## Table of Contents


| | | Page |
|---|---|---|
| 1.0 | BACKGROUND | 1 |
| 1.1 | EPA Regulations Concerning Calibration Gas Accuracy | 1 |
| 1.2 | What are NBS Standards, and How Are They Used to Make Accurate Gases? | 2 |
| 1.2.1 | NBS Weight Standards | 2 |
| 1.2.2 | NBS Gas Standards | 2 |
| 1.3 | EPA Efforts to Help States Obtain Accurate Gases | 4 |
| 2.0 | DISCUSSION | 5 |
| 2.1 | Selecting Components | 5 |
| 2.1.1 | Propane and Hexane | 6 |
| 2.1.2 | Diluents | 8 |
| 2.2 | Concentration of I/M Calibration Gases | 9 |
| 2.2.1 | Warranty Requirements | 9 |
| 2.2.2 | State Requirements - $CO_2$ Concentration | 10 |
| 2.2.3 | State Requirements - Carbon Monoxide - Propane Interference | 10 |
| 2.3 | Cylinders and Hardware | 11 |
| 2.4 | Cylinder Labels and State Audits | 12 |
| 2.5 | EPA Audits | 13 |
| 3.0 | RECOMMENDATIONS | 13 |


## Appendices


Appendix 1 Emission Performance Warranty Regulations Pertaining to Calibration Gases

Appendix 2 Carbon Monoxide - Propane Interference

## 1.0 BACKGROUND

Inspection and Maintenance (I/M) programs are now fully operating in seventeen States, and other States are expected to implement I/M programs in the coming months. Many I/M managers are concentrating on implementing and refining program quality assurance procedures so that motorists can obtain fair and accurate tests of their cars' emissions.

One of the benchmark quality assurance procedures which will be used by every I/M program is the periodic check of every inspection analyzer with a calibration gas of known concentration. This is the only method of checking how accurately a given analyzer is reading vehicle exhaust emissions. The calibration check is performed by flowing the calibration gas into the analyzer and determining whether the analyzer is reading this calibration gas correctly. If the analyzer is not reading this calibration gas accurately, then a simple adjustment of the analyzer can usually be performed which will result in the analyzer being accurate again.

For gas calibration checks and related adjustments to be done properly, the accuracy of the calibration gas used is critical. However, because of a lack of standard procedures in the gas blending industry, it is not safe for the I/M manager to assume that calibration gases have been named properly and are traceable to known standards (NBS). If the labeled concentration of the calibration gas is significantly different from the true concentration in the cylinder, the analyzer could become significantly misadjusted. Furthermore, an operator who had performed the calibration would be unaware that he/she had actually misadjusted the analyzer, since he/she trusted the label on the calibration cylinder to be correct.

In light of its potential significance, EPA has been working with the gas industry over the past several years to identify a way to resolve this problem. The result of these activities is the Recommended Practice which is referred to in this report and discussed in detail in the parallel report ("EPA Recommended Practice for Naming I/M Calibration Gases," EPA-AA-TSS-83-8-B).

### 1.1 EPA Regulations Concerning Calibration Gas Accuracy

In 1980 the EPA promulgated Emission System Performance Warranty Regulations for 1981 and later vehicles which entitle a vehicle owner to emission-related repairs at the manufacturer's expense if, among other things, the vehicle fails an "approved" emission short test. One condition is that the analyzer used to conduct the emission short test

must be checked with gases "traceable to NBS [National Bureau of Standards] standards ±2%" at least once per week. (See Section 85.2217, 45 FR 34808, May 22, 1980. The relevant portion of this page is provided in Appendix 1 to this document.) Many States implementing I/M programs will want to meet the quality assurance requirements of the Warranty regulations so that eligible consumers participating in their I/M programs will have the benefit of receiving warranty repairs from the automobile manufacturers. These States must make sure that the gases used to periodically calibrate analyzers used in their I/M programs meet the regulatory requirement of having an accuracy of ±2% to NBS standards.

## 1.2 What Are NBS Standards and How Are They Used to Make Accurate Calibration Gases?

A standard is an object to which other similar objects are compared. The National Bureau of Standards takes the utmost care in maintaining in-house standards of many different kinds. The standards of concern in obtaining accurate calibration gases are weight standards and gas standards. These standards can be used in a variety of ways in obtaining accurate calibration gases. Some of these ways are better at obtaining accurate calibration gases than others.

### 1.2.1 NBS Weight Standards

NBS weight standards can be used in making accurate calibration gases by weighing in certain masses of calibration gases into a cylinder. For example, a cylinder with a desired concentration of 1000 ppm carbon monoxide (CO) in nitrogen might require 300 grams of CO to achieve that concentration. The cylinder is first emptied and then weighed with a scale calibrated with the NBS weights. The 300 grams of CO are then pumped into the cylinder. Then nitrogen is added to the cylinder in a certain weight to yield the 1000 ppm CO with an appropriate pressure. The CO mixture might then be considered partly "traceable to NBS" via the NBS weight standards. At least some members of the gas manufacturing industry do not consider a mixture made with this method to be entirely "traceable to NBS". They feel that the mixture should be compared to some NBS gas standards using a gas analyzer before the mixture is considered "traceable to NBS". EPA agrees that a mixture made solely using the weight-based method is not "traceable to NBS", particularly as that phrase was intended in the Warranty regulations.

### 1.2.2 NBS Gas Standards

The National Bureau of Standards tries to make available standard gases in commonly requested concentrations. Until

1981, the only NBS standards available were called Standard Reference Materials (SRM's). SRM's have a maximum analytical uncertainty of ±1% to the true value of the concentration in the cylinder. The analytical uncertainty is usually less than ±0.5% of true value.

EPA has required SRM's as the standards to which calibration gases used in many mobile and stationary source programs have to be traced. This created a large demand for SRM's since the tracing process consumes the SRM's. Also, the analysis procedures for SRM's are very detailed and lengthy. These two factors have resulted in SRM's being in short supply. To alleviate this problem, the EPA Emission Monitoring and Support Laboratory at Research Triangle Park (EMSL-RTP) and NBS jointly developed procedures that would allow gas manufacturers to make a new kind of standard, called a Certified Reference Material (CRM), which if made properly has a maximum uncertainty of about ±1.3% to true value. These CRM's can be made in batch quantities, but a limitation of these CRM's is that their concentrations cannot be more than about ±1% different from current SRM concentrations. These CRM's are themselves NBS standards, and a gas mixture which is traceable to a CRM is "traceable to NBS".

NBS gas standards can be used in making I/M calibration gas by comparing the standards to an I/M gas mixture after the I/M gas mixture has been blended into a cylinder. Usually the instrument being used to analyze a mixture is calibrated or checked with NBS gas standards first, then the instrument is used to determine the concentration of the subject mixture. The mixture is then considered "traceable to NBS" since NBS standards were used to calibrate or check the instrument used in analyzing the I/M gas.

Generally, gas manufacturers agree that the method of demonstrating traceability between a gas mixture and NBS gas standards is a better method than the weighing technique, when NBS gas standards exist for a given gas mixture,* because of several possible sources of errors in the latter. (For instance, in the weighing method improper evacuation of the cylinder prior to filling can cause the concentration of the cylinder to be significantly different from its intended concentration. Errors can also occur in the filling process.) However, even though there is agreement that the gas standard comparison procedure is probably best, there is

---

* There are no NBS gas standards for hexane, therefore traceability to NBS within the Recommended Practice can only be obtained with the weighing technique. The Recommended Practice requires hexane gases to be checked with a gas analyzer against the manufacturers' gravimetric (i.e., weighed-in) primary hexane standards.

little agreement among manufacturers about what analytical techniques are best when comparing NBS gas standards with other gas mixtures. These different analytical procedures and methods of handling data may cause differences in the concentrations of identically labeled calibration gases made by different manufacturers or even by the same manufacturer. I/M managers would find it difficult to detect these differences and identify which gas cylinders were correctly labeled, unless they maintain a sophisticated gas analysis program of their own.

### 1.3 EPA Efforts to Help States Obtain Accurate Calibration Gases

In order to improve the general quality of I/M programs and to help States in meeting the calibration gas accuracy requirement of the Warranty regulations, EPA has developed a standard procedure which can be used to accurately name calibration gas traceable to NBS. In a separate report, entitled "EPA RECOMMENDED PRACTICE FOR NAMING I/M CALIBRATION GASES" (EPA-AA-TSS-83-8-B), the "Recommended Practice," which individual States can require gas manufacturers to follow in naming and labeling calibration gas for their I/M programs, is outlined in detail. A State requirement could be imposed by the State in its own purchases of gas and by establishing rules and regulations which require other I/M gas users (contractors or licensed inspection stations) to buy only gas that the manufacturer certifies to be named and labeled according to the Recommended Practice. Such a requirement would assure consistent gas quality among both manufacturers and inspection stations.

Because of the lack of agreement among gas manufacturers as to the analytical procedures for tracing gas mixtures to NBS standards, EPA has taken the initiative in selecting a single set of procedures which it believes represents a good compromise between cost and quality. A special effort has been made to make these procedures workable from a gas manufacturer's viewpoint. A meeting of representatives of the gas manufacturing industry, the National Bureau of Standards and the EPA was held to decide on the original framework of the procedures. Manufacturers have also been allowed to comment on the draft forms of the Recommended Practice, and many of their comments have been incorporated into the procedures.

## 2.0 DISCUSSION

### 2.1 Selecting Components of I/M Calibration Gases

The primary criterion for the user to consider in deciding which components to include in the calibration gas is the kinds of pollutants measured in the I/M program. Some I/M programs measure only for CO emissions; most measure both HC and CO; and a few measure HC, and/or CO, and $CO_2$. Whenever a particular pollutant is measured, then the analyzer accuracy for that pollutant should be periodically verified with a calibration gas.

In those I/M programs which measure only CO, the State may feel that it is necessary only to calibrate analyzers with a CO calibration gas. However, because inspection analyzers also measure the HC in the exhaust, and because mechanics use these HC measurements along with CO measurements for tune-up adjustments and for diagnosing problems causing high emissions and/or poor fuel economy, EPA recommends that the State also require periodic calibration checks of the HC channel of the analyzer. EPA feels that the extra cost of calibrating for both HC and CO is not significantly greater than the the cost of calibrating for only CO and that this cost is greatly outweighed by the benefits of better quality of service to the public.

Some States are also requiring the measurement of $CO_2$ in order to ensure that emission measurements are not biased by improper probe insertion depth or exhaust system leakage, both of which may cause dilution of exhaust gases and, thus, lower emission readings. Whenever $CO_2$ measurements are required, the State should also require periodic calibration checks of the $CO_2$ channel with a $CO_2$ calibration gas. In this case, the issue arises as to whether the $CO_2$ gas should be included along with HC and CO (and diluent) in the same cylinder or whether the $CO_2$ gas should be obtained in a separate cylinder. At the heart of this issue is the basic traceability issue. Introducing $CO_2$ into the HC/CO/diluent blend greatly changes the viscosity of the mixture thereby confounding analysis of the HC component by the flame ionization technique (which is currently the best technique for traceability for HC). There is also an interference effect between measurements of CO and $CO_2$ using the non-dispersive infrared technique, thus confounding analysis of these two components. These problems can be overcome by performing gas analysis using gas chromatography.

Some proponents of $CO_2$ inclusion in the calibration gas mixture argue that because $CO_2$ is a normal constituent of auto exhaust, there is some degree of $CO_2$ interference in the I/M analyzer's CO readings. They conclude, therefore, that it would be beneficial to have $CO_2$ in the calibration

gas so that the calibration gas would more closely simulate auto exhaust. Again, establishing traceability, as discussed above, is a basic problem. Another consideration here is that the amount of $CO_2$ in auto exhaust varies between 6 and 14%, depending on the condition of the vehicle and whether an air pump and/or catalytic converter is used on the vehicle. Because this variability is unpredictable among vehicles, including $CO_2$ (one specific concentration) in the calibration gas is just as likely to introduce new errors as it is to correct existing ones.

In light of the above, EPA recommends that all States use calibration gases which include HC and CO. For those States which require $CO_2$ measurements, EPA recommends that the $CO_2$ calibration gases be obtained in separate cylinders unless the traceability issues discussed above can be adequately addressed.

Two side issues related to selecting calibration gas components are discussed below. Section 2.1.1 discusses the hexane versus propane issue, and Section 2.1.2 discusses the issue surrounding the choice of diluents.

2.1.1 Propane versus Hexane

Even though analyzers measure HC emissions in terms of hexane, analyzers have traditionally been calibrated with propane. This is because propane is an easier gas to work with and is more commercially available.

Because propane is the traditional calibration gas and the analyzer actually measures only the "hexane equivalent" of all non-hexane gases, analyzer manufacturers must establish, during the manufacturing process, a ratio called the propane equivalency factor (PEF) for each analyzer they build. An analyzer's PEF defines the optical relationship between propane and hexane for that particular analyzer's optical bench. PEF values generally range from 0.48 to 0.56 for good quality I/M analyzers. An analyzer which has a PEF of 0.52 will provide a reading of 520 ppm HC (measured as hexane) when calibrated properly and checked with a calibration gas with a concentration of 1000 ppm propane. (The general formula is: Analyzer Response (hexane) = PEF x Calibration Gas Concentration (propane).) This kind of calculation has to be performed each time an analyzer is checked for calibration.

Some I/M program officials feel that it is more appropriate to use hexane as the calibration gas and, thus, to avoid having to perform the PEF calculations and the possible

arithmetic errors associated with them. In addition,there is concern that the PEF value for a particular analyzer may change during the analyzer's useful life.

There are two constraints which make the use of hexane as a calibration gas more difficult than using propane. First, hexane has a low vapor pressure which causes it to condense on the cylinder walls at certain combinations of temperature and concentration levels. Table 1 illustrates the relationship of temperature and concentration at a normal cylinder pressure (for a class 1-A cylinder) of 2000 psi.

Table 1

Theoretical Dew Point Temperatures of
Certain Hexane Concentrations at 2000 psi

| Dew Point Temperature | Hexane Concentration |
|---|---|
| 81°F | 1600 ppm |
| 61°F | 1000 ppm |
| 43°F | 600 ppm |
| 28°F | 400 ppm |
| 7°F | 200 ppm |
| -15°F | 100 ppm |

The proper interpretation of the information in Table 1 is that, theoretically, a mixture of 600 ppm will begin to condense if the temperatures falls below 43°F. Conversely, at a temperature of 43°F, mixtures of hexane with concentrations greater than 600 ppm will condense to some extent. The cylinder pressure is also a factor in this relationship. If the cylinder pressure is less than 2000 psi, as assumed to develop Table 1, the dew point temperatures would be lower for the hexane concentrations listed in Table 1, and the concentrations would be higher for the temperatures listed.

For instance, a mixture of 1000 ppm hexane at 1000 psi would have a theoretical dew point of about 34°F. A mixture of 1600 ppm hexane at 500 psi would have theoretical dew point of about 28°F. Thus, by limiting cylinder pressure to these values and maintaining constant temperatures above the freezing point of water, gas manufacturers can blend stable mixtures of hexane at these higher concentrations. The trade-off, however, is a reduced amount of calibration gas in each cylinder purchased, since the volume of gas in a cylinder is directly proportional to the cylinder pressure. At 500 psi, for example, only one-quarter as much calibration gas can be stored in a cylinder as in the same cylinder at 2000 psi.

The condensation effects of hexane are not as troublesome for the smaller, disposable cylinders, which have a maximum cylinder pressure of 300 psi or less. At this pressure, a mixture of 1600 ppm hexane has a theoretical dew point of about 10°F, and lower concentration mixtures would have even lower dew points. Of course, the cost per volume of gas is higher for these smaller cylinders.

If hexane calibration gases are used, it is necessary to take adequate precautions during gas shipments, storage and use to make sure that the cylinders are never exposed to temperatures below their dew point level. If a lower temperature limit of 43°F were set, the working range of hexane calibration gases in the field would be about 200 ppm to 500 ppm hexane (in 1-A cylinders). However, many areas around the country typically have temperatures below 43°F. For such areas the lower temperature limit would need to be less than 43°F, thus restricting the working range of hexane concentration even more. The exact hexane value for a particular State would depend on the State's climate during the season of interest. In general, very few problems would be encountered during the summer months in any place in the country. However, during winter months, the use of hexane calibration gases in many States may be very risky.

The second constraint regarding the use of hexane is that, unlike propane, there are no NBS gas standards for hexane. Consequently, hexane traceability must be established through the use of weight standards (sometimes referred to as gravimetrics) and the manufacturer's in-house hexane gas standards which are developed from the weight standards. Traceability to NBS can be established in this manner through careful analysis. (At least one gas manufacturer has already developed in-house gas standards for hexane, but others have not.) Because of this more complex analysis, hexane calibration gases may be slightly more expensive in the short run (for those manufacturers which not yet developed in-house hexane gas standards). However, over the long run, cost differences should disappear as the gas manufacturers perfect and streamline the hexane analysis process.

2.1.2 Diluents (Balance Gases)

The diluent is by far the largest component of the gas mixture. It is the carrier or balance gas in which the gases of interest are mixed to get the desired concentrations. The diluent must be chosen with care to avoid chemical reactions with the other gas components and contamination due to impurities which may confound gas analysis.

Nitrogen is the easiest gas to use as a diluent for I/M calibration gases since it is readily available in very pure

forms. Nitrogen is also the best diluent to use for two reasons. First, nitrogen does not react with HC, CO, or $CO_2$. Second, it creates no interference problems in the gas analysis (naming) process. Purified air, the other possible diluent, on the other hand, is not recommended as a diluent for CO because the oxygen in air causes biases in naming the HC component with a process type total hydrocarbon analyzer. This type of analyzer is commonly used by gas manufacturer to name HC gases. Because of this problem, purified air is not recommended as a diluent for I/M calibration gases.

The I/M gas user needs to be aware of the problems with air as a diluent for one other reason. NBS has available propane gas standards in either nitrogen or purified air as the diluent. In ordering calibration gases, I/M users need to be careful to stipulate that NBS propane gas standards in nitrogen are to be used in the analysis of the HC component of the I/M calibration gas in order to prevent errors in analysis.

## 2.2 Concentrations of I/M Calibration Gases

### 2.2.1 Emission Performance Warranty Requirements

In addition to the accuracy requirement for gases used to check emission analyzers (i.e., ±2% to NBS standards), the Warranty regulations also require the calibration gas to be within certain concentration ranges. Section 85.2217 states that "span gases shall have concentrations either:

(i) Between the standards specified in this subpart and the jurisdiction's inspection standards for 1981 model year light duty vehicles, or

(ii) Be within -50% to +100% of the standards in this subpart."

The standards specified in the Warranty regulations are 1.0% CO and 200 ppm HC (measured as hexane) for the two-speed idle test and 1.2% CO and 220 ppm HC for the idle test or the two-mode loaded test. Some States are using these cutpoints, although many States are choosing standards for 1981 and later vehicles which are less stringent. At this time, the most lenient standards likely to be chosen for 1981+ vehicles are 4.0% for CO and 400 ppm for HC (measured as hexane). Table 2 indicates the required calibration gas concentrations for each of these cases.

Table 2

Required Calibration Gas
Concentrations for Selected I/M Cutpoints

| Cutpoints (CO/HC*) | Cal. Gas Concentration CO (%) | HC (ppm) |
|---|---|---|
| 1.0%/200 ppm | 0.5-2.0 | 100-400 (if hexane)<br>200-800 (if propane) |
| 1.2%/220 ppm | 0.6-2.4 | 110-440 (if hexane)<br>220-880 (if propane) |
| 4%/400 ppm | 0.5-4.0 | 100-400 (if hexane)<br>200-800 (if propane) |

* HC cutpoints are always expressed as hexane, and vehicular HC emissions are always measured as hexane in I/M programs.

Based on the information in Table 2, it is clear that users can meet the gas concentration requirement in the Warranty regulations by limiting their gas orders to concentrations in the ranges of 1.0-2.0% CO and 200-800 ppm propane (or 100-400 ppm hexane).

2.2.2 State Requirements - $CO_2$ Concentration

In those cases where a $CO_2$ calibration gas is required, the $CO_2$ concentration of the calibration gas should approximate the $CO_2$ cutpoint used in the I/M program. Unlike HC and CO where cutpoints generally vary by model year, there is often only one $CO_2$ cutpoint applied to all model years. (Sometimes a State may choose different $CO_2$ cutpoints for vehicles with and without air pumps.) Typical State cutpoints for $CO_2$ are from 4 to 6%.

2.2.3 State Requirements - CO/Propane Interference

In addition to meeting the Warranty requirements for HC and CO calibration gas concentrations, some States may wish to use other concentrations of HC and CO (and $CO_2$) in performing multipoint calibrations on analyzers used in the I/M programs. In these cases, the State would need several cylinders of calibration gases at varying concentrations, all with accuracies of $\pm$2% to NBS standards for best results. However, States should be aware of certain aspects of ordering high concentration (i.e., propane greater than 500 ppm and CO greater than 4.0%) blends of calibration gases. There is a small interference effect between CO and propane at high concentration levels on certain instruments that are

used to name these components. This interference effect is described in detail in Appendix 2. To avoid this interference, when high concentration calibration gases are being blended, gas chromatographic analysis of the components should be used by the gas manufacturer to label the gas after mixing. This is required by the Recommended Practice for cylinders containing greater than 500 ppm propane (or 250 ppm hexane) and 4.0% CO. Failure of the gas manufacturer to do this could result in gases not meeting the accuracy limits of ±2% traceable to NBS. Although there have been no known studies of the degree of interference between CO and hexane, it would be advisable to require gas chromatographic analysis of hexane/CO mixtures of similar concentrations as a precaution. Of course, such mixtures will often not exceed 500 ppm hexane because of the condensation problems discussed earlier.

2.3 Cylinders and Hardware

Gas manufacturers have many different sizes of cylinders they can use for I/M calibration gas mixtures, ranging from very large size 9 1/4" by 60" high pressure cylinders* to the low-pressure disposable cylinders. The major cost of a mixture of calibration gas is not for the raw gases that go into making it, but for the analyses required to make sure it is labeled correctly. Consequently, the large cylinders are much more economical per cubic foot of calibration gas mixture than the small disposables, although the disposables have a lower cost per cylinder.

The Recommended Practice requires that the large 9 1/4" by 60" size cylinders be equipped with CGA-350 valves, and that the disposable cylinders be equipped with 1/4-inch flare-fitting valves. The Recommended Practice does not specify valves for other size cylinders because there are so many different sizes. Furthermore, the 9 1/4" by 60" and the disposables will probably be most commonly used. The Compressed Gas Association (CGA) makes recommendations for valves for other cylinders, consequently, there is uniformity between manufacturers on valve usage in other size cylinders.

Users of the I/M mixtures will need regulators to adjust the delivery pressure of the gas mixture to the analyzer. The uniform specifications for valve sizes for the large and disposable cylinders will allow users to change gas manufacturer suppliers without having to purchase new

* The Department of Transportation (DOT) has specifications for all cylinders used to hold pressurized gases. The DOT designation for this cylinder is 3AA2400. Some manufacturers call this a "K" cylinder; others call it a "1-A" cylinder.

regulators, as long as the same size cylinder is ordered from the new supplier. Regulators may or may not be interchangeable among different size cylinders.

EPA highly recommends the use of dual-stage regulators with all calibration gas mixtures and cylinders instead of single stage regulators. The dual stage regulators allow gas to be delivered to the analyzer at a constant pressure, even though the pressure in the gas cylinder declines as gas is used. The single stage regulators do not have this feature. This feature is important because it helps ensure that the instrument is neither starved nor over-pressurized with calibration gas, when gas is introduced through the probe.

Users may also need additional hardware to connect the gas cylinder to the instrument through the sample cell port and/or probe. However, different analyzer manufacturers have different ways of handling this. Users should discuss with their analyzer suppliers what additional hardware is needed to perform these hook-ups.

To conform to the Recommended Practice, the inside surfaces of all cylinders must conform to the NBS CRM or SRM requirements for preparation, cleanliness, trace materials, composition, coatings, etc. for the gas composition and concentrations used. Also, cylinder valves must conform to the NBS CRM or SRM requirements for preparation, packing materials, cleanliness, composition, etc. for the gas composition and concentrations used.

2.4 Cylinder Labels and State Audits

The Recommended Practice requires gas manufacturers to label gases with the following information:

(i) Cylinder number (except in the use of disposables, where the batch number is required)

(ii) Concentration of propane or hexane (in ppm), CO (in mol%), and $CO_2$ (in mol%) and accuracy specification (i.e., $\pm$2%, $\pm$1.0%, etc.)

(iii) Balance gas

(iv) Analysis date

(v) Cylinder numbers of NBS standards (and primary standards if hexane is present) used in determining instrument calibration curves

(vi) Vendor name

(vii) The statement that "This gas has been named in accordance with the EPA Recommended Practice of September 1983 for Naming I/M Calibration Gas".

In most decentralized programs, State auditors will be visiting all inspection facilities once per month in order to check the facility's inspection analyzer, calibration gas and records. The check of the accuracy of the facility's calibration gas will probably be conducted as follows. The auditor will check the facility's analyzer with the auditor's calibration gas. If the analyzer cannot read the auditor's calibration gas within about ±5% of its labeled concentration, the auditor will check the analyzer with the facility's calibration gas. If the analyzer reads that gas within about ±3%, it may be concluded that either the facility's gas or the auditor's gas has been improperly labeled. If the former, then the information present on each cylinder of gas named according to the Recommended Practice will allow auditors to trace that cylinder back to its manufacturer. Gas manufacturers are required to keep the records of the naming process for each batch of gas named according to the Recommended Practice for at least two years. Through this process, it is possible that other cylinders that had been improperly labeled could be identified and recalled.

## 2.5 EPA Audits

EPA does not think it is necessary to check samples of a batch of calibration gas named according to the Recommended Practice prior to the sale and delivery of cylinders of the batch. However, EPA may from time-to-time order gas mixtures named according to the Recommended Practice from manufacturers through a third party for audit purposes. The results of such audits are likely to be published for public inspection.

## 3.0 SUMMARY

EPA recommends that States should require all gases to be named with the EPA Recommended Practice in order to ensure consistent, traceable calibration gases among gas manufacturers and inspection stations. This should be done by specifying the EPA Recommended Practice by name in licensing regulations, contract provisions, and/or purchase orders.

As pointed out in previous sections of this report, EPA has the following additional recommendations on I/M calibration gases:

1. Gas components should include CO and HC. $CO_2$ calibration gas, where needed, should be purchased in separate cylinders unless the related traceability issues are adequately addressed, in which case the $CO_2$ can be obtained in the same cylinder as the CO and HC.

2. The HC component of the gas should be propane, unless adequate precautions are identified and taken to overcome the climatological factors related to hexane condensation and the traceability issues related to the lack of NBS gas standards for hexane.

3. The diluent for I/M calibration gases should be nitrogen. The diluent for the NBS gas standards used in analysis should also be specified as nitrogen.

4. Gas concentrations should be as follows:

   a. CO: 1.0-2.0%.

   b. HC: 200-800 ppm propane or 100-400 ppm hexane.

   c. $CO_2$: about the same as $CO_2$ cutpoint.

5. For calibration gases with gas concentrations of greater than 500 ppm propane (or 250 ppm hexane) and 4.0% CO, gas chromatographic analysis should be used in the naming process to avoid interference problems.

6. Users may purchase I/M calibration gases in any size container they choose. However, corresponding gauges and other hardware should be selected accordingly. Dual-stage regulators are recommended. All inside cylinder surfaces and valves must conform to the NBS CRM or SRM requirements for preparation, cleanliness, composition, etc. for the gas composition and concentrations used.

# Appendices

Appendix 1

EXCERPT FROM: 45 FR 34808, MAY 22, 1980,

EMISSION PERFORMANCE WARRANTY REGULATIONS

§ 85.2217 Calibrations, adjustments.

(a) Equipment shall be calibrated in accordance with the manufacturers' instructions.

(b) Within one hour prior to a test, the analyzers shall be zeroed and spanned. Ambient air is acceptable as a zero gas; an electrical span check is acceptable. Zero and span checks shall be made on the lowest range capable of reading the short test standard.

(c) Within eight hours prior to a loaded test, the dynamometer shall be checked for proper power absorber settings.

(d)(1) The analyzers shall have been spanned and adjusted, if necessary, using gas traceable to NBS standards ± 2% within one week of the test. These span gases shall have concentrations either:

(i) Between the standards specified in this subpart and the jurisdictions inspection standards for 1981 model year light duty vehicles, or

(ii) Be within −50% to +100% of the standards in this subpart.

(2) For analyzers with a separate calibration or span port, CO readings using calibration gas through the probe and through the calibration port shall be made; discrepancies of over 3% shall require repair of leaks. No analyzer adjustments shall be permitted during this check.

## Appendix 2

### CO-HC Interference Discussion

The EPA and the National Bureau of Standards (NBS) have found that a small amount of interference exists in infrared and total hydrocarbon analyzers between CO and propane at high concentration levels.* NBS conducted a test program in which two tri-blend calibration gases, one at a high concentration and one at a lower concentration, were checked for interference. The concentrations ordered for the high concentration cylinder were 8.0% CO, 2500 ppm propane in nitrogen. The concentrations ordered in the lower concentration cylinder were 2.0% CO, 500 ppm propane.

NBS used a gas chromatograph (GC) to check the concentration of each component in both cylinders. Then a total hydrocarbon (THC) analyzer was used to check the propane values, and a non-dispersive infrared analyzer was used to determine the CO values. The assumption in this technique was that the GC values were closest to the true values. Interference between CO and propane would be seen on the THC and NDIR analyzers, if the values they gave were different from the GC values.

The results of the study are presented in the following table, which shows the differences between methods of analyses.

---

* "A Study of Interference in Trinary Span Gases Calibrated With Binary SRM's", available by writing the Technical Support Staff, U.S. EPA, 2565 Plymouth Road, Ann Arbor, Michigan, 48105.

Levels of Interference
Between CO and Propane

Hydrocarbon Concentration
As Determined By

| Sample | G.C. | THA | % Diff |
|---|---|---|---|
| XA4450 | 496 ±1ppm | 501 ±1ppm | 1% |
| A-013329 | 2474 ±1ppm | 2541 ±1ppm | 2.6% |

Carbon Monoxide Concentration
As Determined By

| Sample | G.C. | NDIR | % Diff |
|---|---|---|---|
| XA4450 | 1.997 ±.004% | 2.002 ±.004% | .25% |
| A-013329 | 7.91 ±.01% | 8.04 ±.02% | 1.6% |

G.C. = Gas Chromatograph
NDIR = Non-Dispersive Infrared Analyzer
THA = Total Hydrocarbon Analyzer

The data in the table indicate that, for the HC readings, there is a substantial amount of interference (2.6%) caused by the high concentration (8.0%) of CO. For the CO readings the degree of interference caused by the high concentration (2500 ppm) of propane is less (1.6%) but still significant.

The Recommended Practice assumes that there is a ±1% interference level between propane and CO for gases intended to be traceable to NBS ±2%, and controls other sources of errors so that overall accuracy remains within ±2%. From the information in the table, it appears that this level of interference can only be assumed at propane levels equal to 500 ppm or less, and CO levels equal to about 4.0% CO or less. If States order higher concentration calibration gases with intended accuracies of ±2% NBS, gas manufacturers must use gas chromatographs to overcome interference in their gas analysis in order to be in accordance with the EPA Recommended Practice.